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MeV Si ion beam modification effects on the thermoelectric generator from $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film

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ABSTRACT

Effective thermoelectric materials and devices have a low thermal conductivity and a high electrical conductivity. The performance of the thermoelectric materials and devices is shown by a dimensionless figure of merit, ZT. The purpose of this study is to improve the figure of merit of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film used as thermoelectric generators. We have deposited the monolayer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film on silicon and silica substrates with thickness of 302 nm using ion beam assisted deposition (IBAD). Rutherford backscattering spectrometry (RBS) was used to determine the total film thickness and stoichiometry. The MeV Si ion bombardments were performed on single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films at five different fluences between 5×10^{13}–5×10^{15} ions/cm^2.The defect and disorder in the lattice caused by ion beam modification and the grain boundaries of these nanoscale clusters increase phonon scattering and increase the chance of annihilation of the phonon. The increase of the electron density of states in the miniband of the quantum dot structure formed by bombardment also increases the Seebeck coefficient and the electrical conductivity. We measured the thermoelectric efficiency of the fabricated device by measuring the cross plane thermal conductivity by the 3rd harmonic (3ω) method, the cross plane Seebeck coefficient, and the electrical conductivity using the Van Der Pauw method before and after the MeV ion bombardments.

1. Introduction

Thermoelectric materials are being increasingly important due to their applications in thermoelectric power generation and microelectronic cooling [1]. Effective thermoelectric materials have a low thermal conductivity and a high electrical conductivity [2]. The introduction of the phonon glass-electron crystal concept by Slack has focused the interest of many researchers on materials called as skutterudites for thermoelectric applications [3]. Skutterudites are cubic crystals (space group Im3, $CoAs_3$ is the prototype) composed of a cagelike structure that have large voids available within the structure [4]. Slack suggested that these voids could be filled with atoms that would be loosely bound and be able to "rattle around" within the cage structure and scatter a large range of phonon frequencies. This scattering could result in the lower lattice thermal conductivity. Moreover, the rare-earth doping through the charge compensation techniques to enhance the electronic properties is performed. A general formula is then $RECo_{4-x}M_xSb_{12-y}Ch_y$, where RE denotes the rare-earth rattling atom, M is a transition metal and Ch is an atom in close proximity to Sb in the periodic table [5]. The performance of the thermoelectric materials and devices is shown by a dimensionless Figure of Merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity [6]. ZT can be increased by increasing S, increasing σ, or decreasing κ. The increase in ZT leads directly to improvement in the energy conversion efficiency of TE generators and in the cooling efficiency of Peltier modules [7]. Ion beam mixing has been widely used for compositional and structural modifications of materials that cannot be easily achieved by other methods [8]. By considering the nanostructure formation by ion bombardment in the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film, we prepared the thermoelectric (TE) generators from the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film at the Alabama A&M University (AAMU), Center for Irradiation of Materials. In this study, we report the effect of MeV Si ions at five different fluences on thermoelectric properties of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film systems.

2. Sample preparation and characterization

We have grown the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film of 302 ± 30 nm thick on silica and silicon substrates using ion beam

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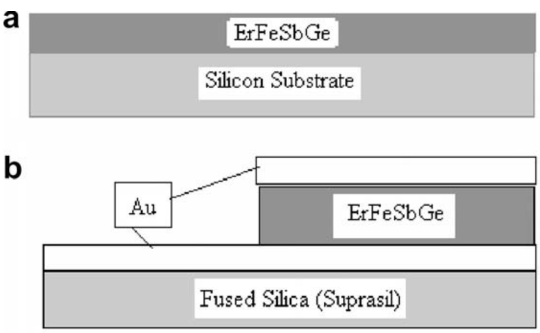

Fig. 1. Geometry of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film from the cross-section for (a) electrical resistivity by Van der Pauw method and thermal conductivity by 3rd harmonic method (b) Seebeck coefficient measurement.

assisted deposition (IBAD). The chamber was maintained at a vacuum of 2×10^{-6} Torr during the deposition. The thickness of the thin films was controlled by an INFICON deposition monitor. The film geometry used for the deposition of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film is shown in Fig. 1. Fig. 1 shows the geometry of the sample from the cross-section for (a) electrical resistivity by Van der Pauw method and thermal conductivity by 3rd harmonic method (b) Seebeck coefficient measurement. As seen from Fig. 1(b), there are two Au contacts on the top and bottom of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film. These two metal (Au) contacts were used for the thermal and electrical contacts during the Seebeck coefficient measurement. The size of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film for Seebeck coefficient measurement is 2×7 mm. The size of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film for electrical and thermal conductivity measurements is 10×10 mm. The electrical resistivity measurements were carried between 300–580 K temperature ranges while Seebeck coefficient (thermopower) measurements were just done at room temperature. Using a Pelletron accelerator at AAMU, a beam of proton ions with energies 5 MeV was scanned sufficiently at room temperature to ensure a homogeneous bombardment on the sample at the vacuum of 1×10^{-7} Torr. The energy of the bombarding Si ions was chosen by the SRIM simulation software (SRIM) [9]. The five different fluences used for the bombardment were 5×10^{13}, 1×10^{14}, 5×10^{14}, 1×10^{15} and 5×10^{15} ions/cm^2. In order to determine the stoichiometry of the each element in the single layer of ErFeSbGe thin film, an identical single layer of ErFeSbGe thin films were grown on a glassy polymeric carbon (GPC) substrate for Rutherford backscattering spectroscopy (RBS) analysis. Rutherford backscattering spectroscopy (RBS) measurement was performed using 2.1 MeV He^+ ions in an IBM scattering geometry with the particle detector placed at 170° from the incident beam to monitor the film thickness and stoichiometry before and after 5 MeV Si ions bombardments [9,10].

3. Results and discussion

He (when the source is He) RBS spectra and RUMP simulation of the as-deposited single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film on a glassy polymeric carbon (GPC) substrate are shown in the Fig. 2. Each element used in the deposition is revealed in the RBS spectra. The RUMP [11] software has been used to specify the composition of each element. RUMP simulation gave the stoichiometry as $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ for the single layer thin film. The measured electrical resistivity values using Van der Pauw technique between 300–580 K temperature ranges are given in the Fig. 3. As seen from Fig. 3, the room temperature resistivity value of unbombarded sample is $4.30 \times 10^{-4}\ \Omega$ cm for the $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ single layer

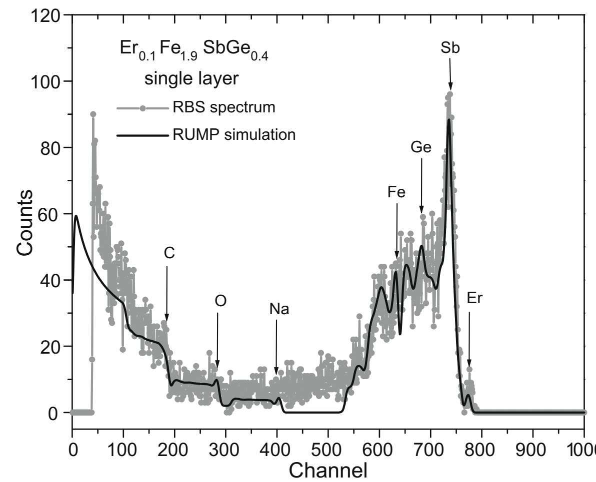

Fig. 2. He RBS spectra and RUMP simulation for the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film on GPC substrate.

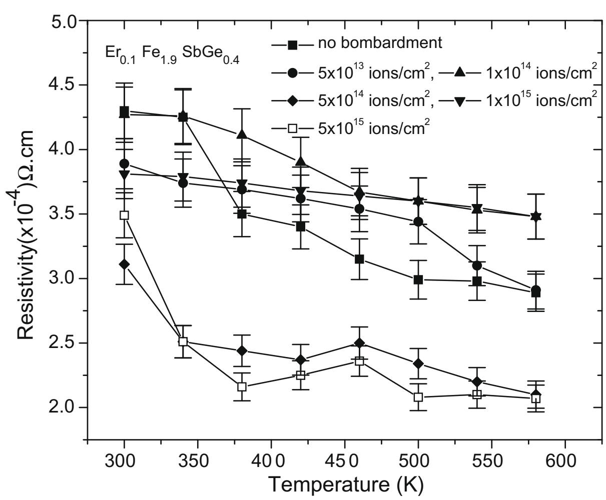

Fig. 3. Electrical resistivity values of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films depending on temperatures.

thin film and the room temperature resistivity values change between the maximum range of 4.30×10^{-4} and the minimum range of $3.11 \times 10^{-4}\ \Omega$ cm for the 5 MeV Si ion bombarded $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ single layer thin films. These values are approximately 5–6 times smaller in the order with respect to Fe and Co based binary and ternary skutterudites [12]. As seen from Fig. 3, while the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films were being bombarded, the electrical resistivity values were decreased for all samples. The ion bombardment seems to cause the narrowing of the energy gap between the conduction and valance bands, therefore allowing for an increased number of majority charge carriers in the material and an increase in the electrical conductivity. The decrease in the electrical resistivity means increase in the electrical conductivity. This is one of the desired properties of the thermoelectric devices and materials [13].

Fig. 4 shows the thermoelectric properties of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films. Fig. 4a shows the fluence dependence of the square of Seebeck coefficients for the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films. For the unbombarded sample of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin film, the Seebeck coefficient (thermopower) is equal to $-30.12\ \mu$V/K. The negative thermopow-

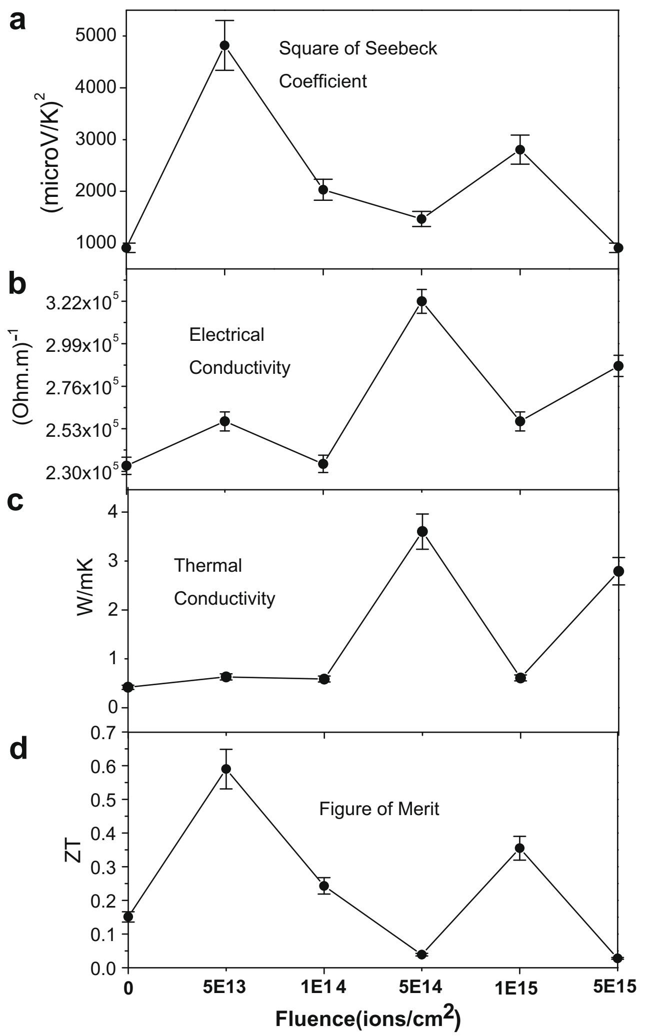

Fig. 4. Thermoelectric Properties of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films depending on fluences.

er values specify the compositions as n-type ternary skutterudites and the electrons are expected to be the main charge carriers in the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films. The Seebeck coefficient increased until -69.43 μV/K at the fluence of 5×10^{13} ions/cm^2, and then decreased to -38.27 μV/K at the fluence of 5×10^{14} ions/cm^2. After the fluence of 5×10^{14} ions/cm^2, the Seebeck coefficient increased up to -52.96 μV/K at the fluence of 1×10^{15} ions/cm^2. After the fluence of 1×10^{15} ions/cm^2, the Seebeck coefficient decreased to -30.12 μV/K at the fluence of 5×10^{15} ions/cm^2. The increase in the Seebeck coefficient is one of the expected properties of thermoelectric materials and devices. The requirement of a high Seebeck coefficient is natural since it is a measure of the average thermal energy which is carried per charge (electron or hole) [14].

Fig. 4b shows the electrical conductivity change of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films depending on the applied fluence of 5 MeV Si ion bombardments. As seen from Fig. 4b, the electrical conductivity started to increase from the virgin case until the fluence of 5×10^{13} ions/cm^2, and then decreased until the fluence of 1×10^{14} ions/cm^2. After the fluence of 1×10^{14} ions/cm^2, the electrical conductivity increased to the value of 3.22×10^5 $(\Omega\,m)^{-1}$ at the fluence of 5×10^{14} ions/cm^2. After the value of 3.22×10^5 $(\Omega\,m)^{-1}$, the electrical conductivity value decreased until the fluence of 1×10^{15} ions/cm^2 and, then it started to increase again after the fluence of 5×10^{15} ions/cm^2. This shows that ion bombardment caused an increase in the electrical conductivity until one certain fluence was reached. While the virgin sample is being bombarded with the 5 MeV Si ions, the numbers of the charge carriers in both the conduction and valence bands increase. This might cause shorter energy gap between the conduction and valence bands. The shorter energy gap causes increase in the electrical conductivity [13]. Fig. 4(c) shows the thermal conductivity change of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films depending on the fluence of applied 5 MeV Si ions bombardment. As seen from Fig. 4c, the thermal conductivity started to increase until the fluence of 5×10^{14} ions/cm^2. At the fluence of 5×10^{14} ions/cm^2, it got the highest value of 3.6 W/mK. After the fluence of 5×10^{14} ions/cm^2, the thermal conductivity decreased until the value of 0.61 W/mK at the fluence of 1×10^{15} ions/cm^2. After the fluence of 1×10^{15} ions/cm^2, the thermal conductivity increased until the value of 2.79 W/mK at the fluence of 5×10^{15} ions/cm^2. As seen from Fig. 4(b) and (c) of the electrical conductivity and thermal conductivity of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films, the high energy ion bombardments can produce nanostructures and modify the property of the thin films [15], resulting in lower thermal conductivity and higher electrical conductivity when the suitable fluences are chosen. Fig. 4(d) shows the figure of merit change of the single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films depending on the applied fluence. As seen from Fig. 4(d), the figure of merit at virgin case of 0.15 has increased when the first fluence of 5×10^{13} ions/cm^2 was introduced up to 0.59. After the fluence of 5×10^{13} ions/cm^2, the figure of merit value decreased until the fluence of 5×10^{14} ions/cm^2. After the fluence of 5×10^{14} ions/cm^2, the figure of merit increased up to 0.36 at the fluence of 5×10^{15} ions/cm^2. As seen from Fig. 4, our thermoelectric properties have been affected from the ion beam bombardment. We expect low thermal conductivity, higher electrical conductivity and higher figure of merit. Depending on the applied suitable fluence, we could be able to get some expected parameters.

4. Conclusion

The single layer of $Er_{0.1}Fe_{1.9}SbGe_{0.4}$ thin films have *n*-type of Seebeck coefficients which were increasing at more or less magnitude with the increasing amount of suitable fluences. Electrical resistivity values are approximately 5–6 time smaller in the order with respect to Fe and Co based binary and ternary skutterudites [12]. That means that the electrical conductivity values are really high with respect to them. The MeV Si ion bombardments at different fluences have affected the electrical conductivity. As the electrical conductivity values were increasing while the bombardment fluences were increasing. The defect and disorder in the lattice caused by bombardment and the grain boundaries of these nanoscale clusters might increase phonon scattering and increase the chance of annihilation of the phonon. The increase of the electron density of states in the miniband of the quantum dot structure formed by bombardment also increases the Seebeck coefficient and the electrical conductivity [16]. The high energy ion bombardment can produce nanostructures and modify the property of thin films [15], resulting in lower thermal conductivity and higher electrical conductivity at the suitable fluences.

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References

[1] S. Budak, C. Muntele, B. Zheng, D. Ila, Nucl. Instr. and Meth. B 261 (2007) 1167.
[2] B.C. Scales, Science 295 (2002) 1248.
[3] G.A. Slack, in: D.M. Rowe (Ed.), CRC Handbook of Thermoelectrics, CRC, Boca Raton, FL, 1995, p. 407.
[4] I. Oftedal, Z. Kristallogr. 66 (1928) 517.
[5] G.A. Lamberton, R.H. Tedstrom, T.M. Tritt, G.S. Nolas, J. Appl. Phys. 97 (2005) 113715.
[6] B.Y. Yoo, C.-K. Huang, J.R. Lim, J. Herman, M.A. Ryan, J.-P. Fleural, N.V. Myung, Electrochem. Acta 50 (2005) 4371.
[7] H.J. Goldshmid, in: T.M. Tritt (Ed.), Recent Trends in Thermoelectric Materials Research I: Semiconductors and Semimetals, Academic Press, New York, 2001, p. 1.
[8] B. Park, F. Spaepen, J.M. Poate, D.C. Jacobson, F. Priolo, J. Appl. Phys. 68 (1990) 4556.
[9] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping Range of Ions in Solids, Pergamon Press, New York, 1985.
[10] W.K. Chu, J.W. Mayer, M.-A. Nicolet, Backscattering Spectrometry, Academic Press, New York, 1978.
[11] L.R. Doolittle, M.O. Thompson, RUMP, Computer Graphics Service, 2002.
[12] J.-P. Fleurial, T, Caillat, A. Borshchevsky, in: Proceedings of the 16th International Conference on Thermoelectrics, Dresden, Germany, 1997.
[13] S. Budak, C.I. Muntele, R.A. Minamisawa, B. Chhay, D. Ila, Nucl. Instr. and Meth. Phys. Res. B 261 (2007) 608.
[14] G. Chen, A. Narayanaswamy, C. Dames, Superlattice. Microstr. 35 (2004) 161.
[15] D. ila, R.L. Zimmerman, C.I. Muntele, P. Thevenard, F. Orucevic, C.L. Santamira, P.S. Guichard, S. Scheisel, C.A. Carosella, G.K. Hubler, D.B. Poker, D.K. Hensley, Nucl. Instr. and Meth. B 191 (2002) 416.
[16] B. Zheng, S. Budak, R.L. Zimmerman, C. Muntele, B. Chhay, D. Ila, Surf. Coat. Technol. 201 (2007) 8531.